

Non-equilibrium Thermodynamics approach to Transport Processes in Gas Mixtures

Z. Hens and X. de Hemptinne

*Department of Chemistry, Catholic University of Leuven,
Celestijnenlaan 200 F, B-3001 Heverlee, Belgium*

The thermodynamic approach to non-equilibrium dynamics describes the state of macroscopic systems by means of a collection of intensities or intensive variables. The latter are by definition the differentials of the entropy with respect to the set of extensive constraints. The environment is directly involved in controlling the intensities. The isolation paradigm is negated. The general principles substantiating the approach are restated and expanded to multi-component systems. The procedure is applied to the prediction of transport processes (viscosity and thermal conductivity) of mixtures of atomic gases. Theoretical results are compared with published experimental data.

I. INTRODUCTION

Excepting recent work centred on trajectory calculations [1,2], the common parenthood of most theoretical approaches to the evolution of irreversible phenomena traces back to Boltzmann's dynamic equation [3,4]. The core of the model is based on the isolation paradigm. Interaction with the surroundings is claimed not to be the necessary condition for breaking the correlations representing particular non-equilibrium initial conditions. By contrast, the molecular chaos hypothesis is presumed. Although this has been violently criticized in the early days, there is presently a considerable literature in mathematical physics arguing in favour of this initial assumption [3,5,6]. Some claim that chaotic Hamiltonian dynamics is the key to decorrelation leading to the required molecular chaos conditions [7].

Contrasting with the former, some other schools of thoughts suggest that correlation breaking is a property typically imported from the surroundings [8–10]. They confirm that strictly isolated systems would follow Liou-villian dynamics with conservation of entropy. The apparent success of Boltzmann's equation and its different approximations is claimed to result from its *a priori* introduction of the molecular chaos assumption. The latter masks or hides non-Hamiltonian dissipative components equally present in the global dynamics, as the effect of unavoidable interactions with the external world [11,12].

One of the arguments of the followers of the isolation paradigm is that transport properties characterizing fluid systems and typical of irreversible dynamics (viscosity, thermal conduction etc.) are bulk properties, whereas interaction with the environment is a surface phenomenon. To this assertion let it be opposed that viscous flow implies the presence of walls, coupled to the system, where

the relevant collective momentum is input or withdrawn. Furthermore, referring to the celebrated Joule experiment, where compressed gas is made to expand spontaneously in an evacuated vessel, it is easy to demonstrate that the initial acoustic shock requires intervention of the walls in order to reach final relaxation. The softer the walls, the faster does the acoustic perturbation vanish. In the unphysical extreme hypothesis where no coupling at all to the environment would exist, not even that represented by action of the ubiquitous electromagnetic radiation field (black body), the system's dynamics would be governed by its only conservative Hamiltonian. The motion would then retain at all times the memory of its initial conditions.

Considering that the dynamics of irreversible processes implies necessarily at some stage action of the surroundings, a general procedure has been developed that quantifies the latter's most relevant properties. This is conveniently done by referring to thermodynamics, to be extended to conditions out of equilibrium. Thermodynamics opens indeed the door to the definition of intensive variables conjugate to every extensive property. For given properties, differences of the intensities in and out the system measure how much the system and its environment are removed from their mutual equilibrium conditions. The procedure has been elaborated and discussed extensively elsewhere [11–14]. It has been applied successfully to a manifold of simple relaxing systems and to systems supporting steady transport of extensive properties (energy, momentum etc.). It has been shown to remain valid in conditions far removed from equilibrium, even beyond predicted bifurcations. The present work expands some of the early results to mixtures of gases and compares the theoretical expectations to published experimental data.

In the traditional approach by Boltzmann and his followers, unbound free flow implies the usage of a Lagrangian description to formalize the motion [15]. That is why, using symbol f to represent the distribution function in phase space, and omitting extraneous forces for simplicity, Boltzmann's dynamic equation is written [9]

$$\frac{\partial f}{\partial t} + \sum_k v_k \frac{\partial f}{\partial x_k} = C(f), \quad (1)$$

where C represents the collision integral. The resulting distribution functions are time dependent, even in stationary conditions [16], leading to physically less transparent conclusions. By contrast, by referring relaxing systems to their fixed boundaries and considering local

thermodynamic properties, the thermodynamic approach fits remarkably in an Eulerian frame [15,17]

$$\frac{df}{dt} = [f, H] + J. \quad (2)$$

In the latter equation, $[f, H]$ is the Poisson bracket describing the implicit motion while J is a source/sink term expressing explicit action of the environment. Integrating the equation yields very simple expressions for the relevant distribution functions. In stationary conditions the distribution functions are time independent. This is a great advantage of the procedure.

The present contribution is structured as follows. General principles supporting thermodynamics of systems out of equilibrium are outlined in section 2. The formalism leading to prediction of transport properties is developed in section 3, where it is applied to single component dilute gases. Extension towards mixtures of the atomic gases and comparison with published experimental data is the subject of the last section.

II. THERMODYNAMICS OUT OF EQUILIBRIUM

It is impossible to specify exactly the state of a complex macroscopic system (macrostate). We must content ourselves with descriptions that are considerably less than complete. In fact, our exact information about the properties of many-particle systems is restricted to a small number of mechanical observables or constraints, directly related to the system's Hamiltonian. Among others, let us quote: the number of particles of any sort (j): N_j , the total energy E and the accessible physical volume V . That are the traditional micro-canonical constraints or extensive variables. In non-equilibrium conditions, additional constraints prevail, like the total linear momentum \mathbf{P} , the total angular momentum and also possible momenta of all the properties cited above.

A. The Entropy

Any function determined completely by the set of constraints describing its particular macrostate is a function of state. The theoretical definition of the function of state *entropy* goes back to Boltzmann.

$$S = k_B \ln[W(A)]. \quad (3)$$

For the inventor, $W(A)$ meant “wahrscheinlichkeit” which is probability. Digging for the realities hidden behind this word may lead to some controversies but, using the same initial letter, most authors wisely prefer the English *weight of the given observational state or macrostate*. The latter is interpreted as the measure of the domain accessible to the motion in phase

space, given the set of constraints (represented here by the collective variable A) describing the system's particular macrostate. An equivalent definition for $W(A)$ is the number of quantum states (= microstate) all compatible with the given set of constraints. Let it be stressed that Boltzmann's definition is applicable to non-equilibrium conditions simply by including the additional constraints in the definition.

Let the list of the extensive constraints defining a given macroscopic system in a particular macrostate be written $\{X_r\}$. The entropy is a function of this collection of variables. By differentiating with respect to this set we get by definition the set of conjugate intensive variables or intensities $\{\xi_r\}$.

$$dS = \sum_r \frac{\partial S}{\partial X_r} dX_r = -k_B \sum_r \xi_r dX_r. \quad (4)$$

Equation (4) is Gibbs' celebrated differential equation, generalized to possible non-equilibrium conditions. It renders the usual temperature $(\partial S/\partial E)^{-1}$ and the collection of chemical potentials $-T(\partial S/\partial N_j)$. In non-equilibrium conditions it generalizes the definition by attaching a given intensity to each of the additional non-equilibrium constraints.

Boltzmann's definition of the entropy is valid whatever the number of particles in the system of interest. A significant advantage of referring to its differentials, namely the intensities, is that their values are independent of this number and also of the discrete nature of physical systems.

B. Generalized Massieu function

If two systems are allowed to exchange some extensive properties it is easy to show that the state of mutual equilibrium, that is the condition where exchange vanishes on the average, occurs when the conjugate intensities equalize [18]. The total entropy becomes then insensitive to possible infinitesimal fluctuations in the relevant exchange [12].

Let the two systems to be considered be a huge body representing the surroundings (reservoir) on one hand and a small object called the system on the other. Their respective dimensions are such that thermodynamic flows do not alter significantly the reservoir's intensive variables. The latter are therefore constants, defining the external experimental parameters and fixing the constraints imposed to the smaller system. Intensities are indeed better measured and controlled. Therefore, instead of referring to the entropy, an explicit function of the extensive properties ($\{X_r\}$), thermodynamics makes widely use of thermodynamic potentials and Massieu-Planck functions, obtained from the extensive properties by Legendre transformations [19].

The constant volume Legendre transform of the entropy is the generalized Massieu function $\mathcal{M}(V, \xi_r)$. It is

obtained by performing the following transformation on the entropy:

$$\mathcal{M}(V, \xi_r) = \frac{S}{k_B} + \sum_r \xi_r X_r, \quad (5)$$

whereby the volume is not included in the collection of indexed constraints.

Differentiating \mathcal{M} with respect to any intensive variable yields readily the conjugate extensive properties.

$$X_r = \frac{\partial \mathcal{M}}{\partial \xi_r}. \quad (6)$$

C. Dilute Gases

With ideal gases, the expression for the generalized Massieu function takes a very simple form. Individual particles assumed to be independent, the global motion may be represented by a swarm of points in a reduced $6N$ -dimensional single-particle phase space (Γ) .

Let $f(\Gamma)$ be a particle distribution function. Any extensive property X_r may then be related to a generating function $\phi_r(\Gamma)$ so that

$$X_r = \int_{\Gamma} \phi_r(\Gamma) f(\Gamma) d\Gamma. \quad (7)$$

With that formalism, using the Lagrangian multipliers procedure to specify the maximum entropy conditions compatible with the set of constraints, it is easy to show [12] that function $f(\Gamma)$ becomes

$$f(\Gamma) = \exp\left[\sum_r \xi_r \phi_r(\Gamma)\right]. \quad (8)$$

With ideal gases, if equation (5) is implemented with the two latter expressions, \mathcal{M} takes the very simple form

$$\mathcal{M}(\xi_r, V) = \int_{\Gamma} \exp\left[\sum_r \xi_r \phi_r(\Gamma)\right] d\Gamma. \quad (9)$$

The numerical value of this function is the (average) number of particles contained in the system. Through the integration limits in configuration space it has the system's physical dimensions (volume) as one of its independent variables. By restricting the integration to the only momentum coordinates, a local generalized Massieu function is obtained, the value of which represents the average local density in configuration space.

With real gases, the generalized Massieu function is modified due to the interaction potential between the particles. The simplified formulation is however still useful as an approximation in low density conditions, when the duration of the inter-particle collisions is negligible compared to the time separating collisions. With hard spheres this is certainly the case.

III. TRANSPORT COEFFICIENTS

One of the main objectives of the theoretical approach to non-equilibrium dynamics is the prediction of transport coefficients from first principles. Comparison between the predicted and experimental results is often considered as a test for the validity of the relevant attempt.

Since Boltzmann first proposed his kinetic equation there has been a considerable literature concerning the calculation of the transport coefficients [20,21]. Most frequently cited are the traditional Chapman and Enskog derivations [16] and the Green-Kubo formalism.

It has been stressed above that, for all but perhaps a few mechanical properties, exchange occurs more or less readily with the surroundings, tending to equalize the conjugate intensities to the reservoir values. This justifies thermodynamic expressions based on intensities. When intensities conjugate to exchangeable properties are different from the reservoir values, we have transient conditions from where the system tends to relax. If the system of interest is connected to a surroundings that is not at equilibrium, it reaches and remains in a stationary state out of equilibrium. This is the condition we shall focus on now.

If the system is interacting with two reservoirs at different temperatures separated by some distance (here: $2D$), the conditions of the surroundings define and dictate to the system the genuine non-equilibrium intensity "temperature gradient". Similarly in the Couette flow problem, the externally imposed gradient is caused by a couple of walls moving in opposite directions. This generates in the system a non-equilibrium intensity "gradient of shear momentum". Asymmetric exchange with the two reservoirs produces flows. In this section, the relevant transport coefficients will be examined using a thermodynamic description. For simplicity, the discussion will however be limited to hard sphere atomic gases.

In extremely low density systems, where the mean free path is comparable or longer than the system's physical dimensions (Knudsen gas), properties picked up by any particle from one wall are transported in a single jump to the opposite wall. Transport is very efficient indeed. In the thermodynamic limit (non-Knudsen regime), head-on collisions of like particles do not slow down the transport properties. By contrast, parallactic or off-axis inter-particle collisions do. Their effect is one of reducing the range of free transport, while information about the conditions prevailing in the external reservoir and available at the boundaries is transferred to the relevant region of the bulk. As a result, local values of the thermodynamic properties are justified.

For the same reason, the flow rates depend on the average periodicity τ of the perturbing collisions.

A. Single component gases

Let us consider an arbitrary property X_r with generating function $\phi_r(\Gamma)$. We assume that its flow is directed along the z -axis. Let us consider a plane positioned at coordinate z^* . The basic equation for the flow J_r of the relevant property through this plane is

$$J_r = \frac{1}{\tau} \iiint \frac{d^3\mathbf{p}}{h^3} \int_{(z^*-p_z\tau/m)}^{z^*} \phi_r(\Gamma) \exp\left[\sum_l \xi_l \phi_l(\Gamma)\right] dz. \quad (10)$$

The symbol $d^3\mathbf{p}$ is a short form for $dp_x dp_y dp_z$. Integration limits in momentum space is $-\infty \rightarrow \infty$. Plank's constant in the numerator represents a norm in phase space, related to the classic- quantum correspondence [18]. In the subsections to follow, this equation will be applied to different types of flow.

It may be useful to stress the difference between equation (10) and that proposed elsewhere, in own relevant different contexts for flows of extensive properties [16,21]:

$$J_r = \int \int \int \frac{p_z}{m} \phi_r(\Gamma) \exp\left[\sum_l \xi_l \phi_l(\Gamma)\right] \frac{d^3\mathbf{p}}{h^3}. \quad (11)$$

Contrasting with the latter, equation (10) confirms that transport occurs during the free motion time separating relaxing collisions. The lesser the collision frequency, the more effective is the transport. Collisions do not activate transport. They do increase resistance to transport.

1. Viscosity

We consider a fluid bound by a pair of walls moving in opposite directions (Couette flow). Excepting negligible higher order corrections (proportional to $\tau^2(\beta m D^2)^{-1}$), the system's conditions are defined completely (at the lowest order in τ) by the set of constraints listed in table I. The intensities under direct control of the surroundings (exchangeable) are the particles number, the kinetic energy and the intensity conjugate to the gradient of shear momentum. It may indeed be verified readily that the velocity of the walls (y - direction) equals $\pm\sigma_y/\beta$. Two variables remain to be determined, namely θ_2 and γ_2 . (Index 2 refers to quadratic moments). They require two independent equations.

In stationary conditions there is no local accumulation of the transverse component of momentum (p_z) (no pressure gradient, no acoustic perturbation). The relevant flow is therefore independent of z^* . Likewise, the total flow of energy through the system is zero. By implementing equation (10) with the two relevant generating functions, the conditions $\partial J_{p_z}/\partial z = 0$ and $J_U = 0$ yield together

$$\theta_2 = 0, \quad \frac{5}{2} \frac{\gamma_2}{\beta} = \frac{m\sigma^2}{2\beta}. \quad (12)$$

The flow of shear momentum may now be determined by implementing equation (10) with the generating function p_y , where θ_2 and γ_2 have been replaced by their values. This yields

$$J_{p_y} = -\frac{\sigma_y}{2\beta D} \frac{n\tau}{\beta}, \quad (13)$$

where $n = \mathcal{M}/V$ represents the particle density.

The phenomenological reaction at the plates' level compensating for transfer of momentum from wall to wall is friction. Shear viscosity is the ratio of the sum of the forces applied to the two plates to the velocity gradient ($\sigma_y(\beta D)^{-1}$). Following equation (13), its value is

$$\eta = n \frac{\tau}{\beta}. \quad (14)$$

2. Thermal conduction

Now we consider a system in thermal contact with a couple of heat reservoirs at different temperatures separated by a distance $2D$. The system's stationary non-equilibrium conditions are completely described (at the lowest order in τ) by the set of constraints listed in table II. By inspecting the generating function conjugate to the temperature gradient it is clear that $k_B \nabla T = -\gamma_1(\beta^2 D)^{-1}$. (Index 1 refers to linear moments).

Knowing that the system is bound by a pair of impervious walls it may look strange that collective motion of the particles perpendicularly to the walls needs to be anticipated in constructing the expression for the non-equilibrium distribution function f (equation 8).

In a system controlled by two heat reservoirs at different temperatures, kinetic energy is not uniformly distributed among the particles. Those moving towards the cold wall have been equilibrated with the system upstream in a hotter region at the instant of their previous collision and vice-versa. In moving from the hot wall to the cold one, particles travel on the average faster than in their return cycle. If the particles are to change their average kinetic energy in a correlated fashion on impact with either walls, while the container (the pair of walls) is to remain immobile, collective momentum is transferred by the container into the system.

The intensities under direct control of the surroundings (conjugate to exchangeable properties or otherwise given constant properties) are the intensity conjugate to the particle number, the temperature (or better β) and the temperature gradient. Two intensities remain to be determined: θ_1 and σ_z . This requires two independent equations. One is the condition for stationarity. The other equation describes mechanical equilibrium of the system between its walls.

According to the local description, at any point in the bulk of the system, the average particles density n responds to the equation

$$n(z^*) = \frac{1}{h^3} \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z \exp\left\{\sum_r \xi_r \phi_r[(z = z^*), \mathbf{p}]\right\}. \quad (15)$$

At any position z^* , we consider the partial density $n_+(z^*)$ of the only particles with positive velocity along the z -direction. Stationarity implies that this partial density is compensated exactly by the sum of the densities of the particles issued from regions from where they will be reaching this position undisturbed in one collision period, their velocities being oppositely oriented ($p \leq 0$). Hence

$$n_-(z^*) = \frac{1}{h^3} \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^0 dp_z \exp\left\{\sum_r \xi_r \phi_r\left[\left(z = z^* - \frac{p_z \tau}{m}\right), \mathbf{p}\right]\right\}. \quad (16)$$

To the lowest order in τ , Relation $n_-(z^*) = n_+(z^*)$ yields

$$\left(\theta_1 - 2\frac{\gamma_1}{\beta}\right) \frac{\tau}{mD} = 2\sigma_z. \quad (17)$$

The second equation expresses position independence of flow of momentum across the system. In other words, there are no pressure gradients. Equation (10) is used with p_z as the flow defining generating function. The condition $\partial J_{p_z}/\partial z = 0$ yields (to the lowest order in τ)

$$\theta_1 = \frac{5}{2} \frac{\gamma_1}{\beta}. \quad (18)$$

Flow of energy (heat) through the system is given by this same general equation (10) where the flow defining generating function is now $\sum(p^2/2m)$. For particles associated with internal rotational motion (Eucken correction [16,22]), the relevant contribution to the energy should be added to the latter generating function. With atomic gases the result reads

$$J_E = \frac{5}{2} \frac{n}{\beta^2} \left[\sigma_z - \frac{1}{2} \left(\theta_1 - \frac{7}{2} \frac{\gamma_1}{\beta} \right) \frac{\tau}{mD} \right]. \quad (19)$$

By implementing the latter with the relevant values of θ_1 and σ_z , flow of energy becomes

$$J_E = \frac{15}{8} \frac{\gamma_1}{\beta^2 D} n \frac{\tau}{\beta m}. \quad (20)$$

Heat conductivity (λ) is defined as the ratio between the sum of the rates of heat exchange at either walls ($2J_E$) and the temperature gradient. Hence

$$\lambda = \frac{15}{4} k_B n \frac{\tau}{\beta m}. \quad (21)$$

In equations (14) and (21) the transport coefficients are expressed in terms of the effective collision periodicity τ . For direct comparison with experimental results, an additional expression is required that relates the collision periodicity to the mechanical properties of the colliding species (mass and cross-section) at the given temperature. Here there remains an uncertainty concerning the model to be adopted for relaxing collisions, yielding the effective cross-section as a function of the temperature. For evaluating the results presented above it is therefore advisable to eliminate the variable τ in the discussion. That is where the Prandtl number comes in. It is related to the ratio between viscosity and heat conductivity and given by

$$Pr = \frac{\eta c_p}{m \lambda}, \quad (22)$$

with c_p as the constant pressure heat capacity. By implementing this definition with the results obtained above, the experimental values are obtained identically, thereby corroborating the general model. [16,21].

B. Mixtures of atomic gases

We are now investigating transport processes in binary mixtures of gases. Let the components be indexed A and B , where A points to the component with the highest mass. Each may be considered as a separate system, with its own thermodynamic functions, interacting simultaneously with the other component and with the environment. The generalized Massieu function being an extensive properties, we have for the composite system

$$\mathcal{M} = \mathcal{M}_A + \mathcal{M}_B. \quad (23)$$

With dilute gases or gases interacting as hard spheres, the individual generalized Massieu functions are defined as in equation (9). For each component separately the generating functions to be used are the same as for single-component gases (see tables I and II), excepting for the additional indexing of the mass of the relevant particles in the generating function for kinetic energy. In stationary or quasi-stationary conditions (see below), for exchangeable properties where equilibrium between the subsystems prevails, the intensities are the same. In the examples treated below, that will be the case for the temperature and its moments and for the intensities conjugate to the collective motion. Intensities conjugate to the populations and their own moments however will be indexed according to which component they refer to.

It has been stressed above that the collision periodicity is an essential ingredient in the dynamics of systems out of equilibrium. In multi-component systems, there is an average collision periodicity for each of the constituents (τ_A, τ_B). It measures for each component how long the relevant atoms move freely before being halted by the matrix formed by the other particles, making them feel

the thermodynamic conditions dictated by the environment.

In multi-component systems there are homogeneous and heterogeneous relaxing collisions. Their frequencies add up. The efficiency for exchange of momentum from a colliding atom to the local thermodynamic bath depends on the masses of the collision partners. When a heavy particle hits a light constituent of the thermodynamic bath, its path is less disturbed and less momentum is transferred than in the opposite case.

We assume a particle with mass m_1 and linear momentum \mathbf{P} hitting a stationary matrix particle with mass m_2 . If the exit path of the matrix particle forms an angle ψ with the incident one, momentum transferred to the matrix equals $2|\mathbf{P}|\cos(\psi)m_2/(m_1 + m_2)$. Hence, the relative transfer efficiency of heterogeneous collisions is $2m_2/(m_1 + m_2)$. For the total effective collision frequency of atoms of one sort with respect to the matrix (the reciprocal of τ), the latter coefficient is the appropriate scaling factor relating the efficiency of heterogeneous collisions to the homogeneous ones.

We take the atoms to be hard spheres. The collision cross-sections are respectively d_{AA}, d_{BB}, d_{AB} . Using the scaling parameter defined above, omitting the common factor $\frac{5}{16}\sqrt{\beta/\pi}$ and adding for either constituents the individual effective collision frequencies, the two total effective collision periodicities read

$$\tau_A \simeq \left(\frac{n_A d_{AA}^2}{\sqrt{m_A}} + \frac{2m_B}{m_A + m_B} n_B d_{AB}^2 \sqrt{\frac{m_A + m_B}{2m_A m_B}} \right)^{-1}, \quad (24)$$

$$\tau_B \simeq \left(\frac{2m_A}{m_A + m_B} n_A d_{AB}^2 \sqrt{\frac{m_A + m_B}{2m_A m_B}} + \frac{n_B d_{BB}^2}{\sqrt{m_B}} \right)^{-1}. \quad (25)$$

Considering that transport coefficients of mixtures are systematically compared or normalized to either one of the pure gas values, the common factor cancels.

For simplifying the formalism it is advisable to replace n_A by xn and n_B by $(1-x)n$. This will be done systematically below.

With hard spheres we have $d_{AB} = (d_{AA} + d_{BB})/2$. It appears that experimental accuracy of the published data on the viscosity of mixtures of atomic gases is sufficient to allow the heterogeneous hard sphere diameter to be corrected by a factor ϵ close to 1.

1. Viscosity

We consider a binary mixture of atomic gases bound by a pair of walls moving in opposite directions (Couette flow). The mole fraction of substance A is written x ($N_A + N_B = N$).

The intensities under direct control of the surroundings (exchangeable properties or otherwise independent properties) are the intensities conjugate to the particle numbers of either substances (α_A, α_B), the temperature (or better β) and the linear moment of shear velocity

σ_y (see table I). Three intensities need still to be determined, namely the quadratic moment of the temperature (or better γ_2) and the quadratic moments of the particle distributions for A and B ($\theta_{2,A}, \theta_{2,B}$).

The three additional relations required for completing the thermodynamic description of the system are of the same vein as those used for Couette flow in single component gases (see above). For symmetry reasons, flow of shear momentum is independent of the particular values of the additional intensities. The principles involved in their determination will therefore be postponed until the section concerning thermal conductivity and diffusion.

Flow of momentum is supported by either components. For each, the contribution is given according to equation (10), where the generating function to be implemented as ϕ_r is p_y . Integration yields

$$J_{p_y} = -n \frac{\sigma_y}{2\beta^2 D} [x\tau_A + (1-x)\tau_B]. \quad (26)$$

The viscosity of the mixture is therefore

$$\eta_{mix} = \frac{n}{\beta} [x\tau_A + (1-x)\tau_B], \quad (27)$$

where n/β is the total pressure (\mathcal{P}).

In figure 1 the result of equation (27), is plotted for a mixture of Xe in He. The experimental results at 291 K published by E. Thornton and coworkers [23] are indicated on the same graph (experimental uncertainties $\sim \pm 1\%$). The correction factor ϵ for heterogeneous collisions may be estimated by fitting the curve to the experimental results. The curve obtained without the correction factor ($\epsilon = 1$) is displayed as a dotted curve.

The same fit has been performed on the ten different mixtures of atomic gases at the same temperature of 291 K. Table III lists the values of ϵ giving the best result for each mixture.

2. Diffusion and thermal conduction

We consider now a binary mixture of atomic gases in thermal contact with a couple of heat reservoirs at different temperatures separated by a distance $2D$. The mole fraction of the heaviest substance (A) is written x .

For each of the two components, the stationary non-equilibrium conditions are completely described by the set of constraints listed in table II. The intensities must be indexed accordingly.

The intensities conjugate to the particle numbers of either substances (α_A, α_B), the temperature (or better β) and its gradient (or better γ_1) are under direct control of the surroundings. Thermal interaction between the subsystems removes the necessity of indexing the latter two intensities.

Three intensities remain to be determined namely the two gradients of the particle distributions ($\theta_{1,A}, \theta_{1,B}$) and the intensity conjugate to the collective momentum

from wall to wall (σ_z). Hence, three additional conditions or equations are needed in order to describe the system completely.

Two of the additional conditions are identical to those discussed for single component systems. It are mechanical equilibrium and stationarity of the total particle distribution.

Mechanical equilibrium of the system between its walls implies vanishing total pressure gradient. It does not require *per se* vanishing pressure gradient for either substances separately. A possible pressure gradient of A is neutralized by an opposite gradient for B . The condition is formalized by stating that the sum of the contributions of either substances to flow of momentum between the boundaries is position independent

$$\frac{\partial J_{p_z,A}}{\partial z} + \frac{\partial J_{p_z,B}}{\partial z} = 0. \quad (28)$$

Applying equation (10) with $\phi = p_z$ for each of the two substances leads to

$$x(\theta_{1,A} - \frac{5}{2} \frac{\gamma_1}{\beta}) + (1-x)(\theta_{1,B} - \frac{5}{2} \frac{\gamma_1}{\beta}) = 0. \quad (29)$$

Let it be stressed that the pressure gradient for A , is

$$\nabla \mathcal{P}_A = \frac{n_A}{\beta D} (\theta_{1,A} - \frac{5}{2} \frac{\gamma_1}{\beta}), \quad (30)$$

with $n_A = xn$, and *mutatis mutandis* for B .

The condition for stationarity is defined along the same lines as above (equations 15–17), where the densities $n_+(z^*)$ and $n_-(z^*)$ are now understood as the sum of the different components. As a result, the relation for internal collective motion (σ_z) becomes (see equation 17)

$$x\sqrt{m_A}[\sigma_z - \frac{1}{2}(\theta_{1,A} - 2\frac{\gamma_1}{\beta})\frac{\tau_A}{m_A D}] + (1-x)\sqrt{m_B}[\sigma_z - \frac{1}{2}(\theta_{1,B} - 2\frac{\gamma_1}{\beta})\frac{\tau_B}{m_B D}] = 0. \quad (31)$$

The last condition to be considered concerns mutual diffusion or motion of the subsystems with respect to each other. By implementing equation (10) with the generating function $\phi_r = 1$ the particle flow of either subsystems is obtained, according to whether the parameters in the exponential function are indexed A or B . The results are

$$J_A = \frac{xn}{\beta} [\sigma_z - \frac{1}{2}(\theta_{1,A} - \frac{5}{2} \frac{\gamma_1}{\beta}) \frac{\tau_A}{m_A D}], \quad (32)$$

$$J_B = \frac{(1-x)n}{\beta} [\sigma_z - \frac{1}{2}(\theta_{1,B} - \frac{5}{2} \frac{\gamma_1}{\beta}) \frac{\tau_B}{m_B D}]. \quad (33)$$

The first contribution in either equations (that proportional to σ_z) represents collective drag generated in the fluid by correlated effect of the two walls. This acts on the two subsystems alike. Therefore it does not drive

diffusion of one subsystem with respect to the other one. By contrast, diffusion is described by the second part of the flow equations. As it may be verified, this is driven by the relevant partial pressure gradient.

Diffusion coupled to flow of heat and vice-versa are known as the Dufour and the Soret effects [16]. Let us consider substance A as the solute and B as the solvent. If transport of heat and matter are expressed using the convenient parameters for the relevant generalized forces (the conjugate intensities, here γ_1 and $\theta_{1,A}$), Onsager's phenomenological equations are retrieved [24,25].

The diffusive stationary state is reached by differential displacement of the subsystems with respect to each other. Then we have for either subsystems vanishing partial pressure gradients. This represents therefore the remaining constraint for complete thermodynamic description of the stationary non-equilibrium system. The question is however how fast the diffusive stationary state may be reached in practical cases when thermal conductivity of multi-component mixtures is measured.

The experimental procedure for measuring thermal conductivity consists in preparing an appropriate binary mixture in equilibrium conditions in a conventional thermostat, the mixture being then introduced between two walls held or brought at different temperatures. When mechanical equilibration is established (relaxation of acoustic perturbations), the total pressure is flat (equation 29). Nevertheless, on transferring the mixture in the region with the temperature gradient, individual pressure gradients on the subsystems may have been created, forcing the particles to segregate. If the mixture consists of particles with different mobility it is expected that establishment of final stationary conditions is slow. The slower moving particles tend indeed to remain distributed homogeneously, as they were before the establishment of the temperature gradient, while the partial pressure gradient of the faster moving subsystem compensates for the former's resulting partial pressure unbalance.

When comparing predicted values of thermal conduction to experimental data, there is uncertainty as to how much the system has been allowed to relax the slow coupled particle segregation in the relevant measurement. Let us assume this would not have occurred at all (pseudo-stationary state). The two subsystems may then be considered as acting independently for all the properties concerning the particle distributions. They remain however tightly coupled for all the properties that are promptly interchanged. In particular, they share the same value of β and γ_1 . The intensity σ_z conjugate to the collective momentum generated by the temperature gradient is also common to the two subsystems. Concerning the latter, its relation to the other intensities and to the collision periodicities is given by equation (17). Instead of equation (31) we have now two relations, namely

$$(\theta_{1,A} - 2\frac{\gamma_1}{\beta}) \frac{\tau_A}{m_A D} = 2\sigma_z, \quad (34)$$

$$(\theta_{1,B} - 2\frac{\gamma_1}{\beta}) \frac{\tau_B}{m_B D} = 2\sigma_z. \quad (35)$$

By combining the equation for overall mechanical stability (equation 29) with the two latter ones, an expression for the gradients of the individual partial pressures may be derived. Writing

$$R = \frac{\tau_A/m_A}{\tau_B/m_B}, \quad (36)$$

this relation reads

$$\theta_{1,A} - \frac{5}{2} \frac{\gamma_1}{\beta} = \frac{1}{2} \frac{(1-R)(1-x)}{(1-x)R+x} \frac{\gamma_1}{\beta}. \quad (37)$$

In practical cases, when heat conductivity is measured, the system may be somewhere between the two extreme conditions. The uncertainty concerning how close diffusion has reached stationarity in the experimental conditions where the measurements have been performed explains why thermal conduction data of mixtures are difficult to reproduce. Let us express the uncertainty by a coefficient c to multiply the right-hand side of equation (37). When discussing a homogeneous set of data with varying compositions x , we assume for simplicity that the same coefficient is valid.

Transport of heat is supported by either components of the mixture.

$$J_E = J_{E,A} + J_{E,B}. \quad (38)$$

For each, the contribution is given according to equation (19), where the relevant intensities are as determined above. Hence,

$$J_E = \frac{xn}{\beta^2} \left[\sigma_z - \frac{1}{2} \left(\theta_{1,A} - \frac{7}{2} \frac{\gamma_1}{\beta} \right) \frac{\tau_A}{m_A D} \right] + \frac{(1-x)n}{\beta^2} \left[\sigma_z - \frac{1}{2} \left(\theta_{1,B} - \frac{7}{2} \frac{\gamma_1}{\beta} \right) \frac{\tau_B}{m_B D} \right]. \quad (39)$$

In comparing the result with experimental data, coefficient c may be taken as an adjustable parameter. This exercise has been performed on the data at 291 K published by E. Thornton and coworkers [26]. The coefficients yielding the best fit are listed in table IV. Figure 2 is an illustration of the results. The accuracy is better than the announced experimental precision (4%).

IV. CONCLUSION

The theory for transport of extensive properties in dilute mixtures of atomic gases has been successfully developed in the context of the thermodynamic approach to non-equilibrium processes [12]. The equations are based on accurate definitions of intensities conjugate to the set of extensive properties defining the system's particular macrostate. Intensities are the natural parameters for

external control of macroscopic systems. It may therefore be claimed that the procedure presented above is characterized by a greater physical transparency when compared with the traditional treatments [16]. The number of adjustable parameters it implies is low and their physical meaning is straightforward.

The theory confirms that inter-particle collisions are not responsible for the transport processes. By contrast, transport occurs during the free motion time of the particles in the periods separating collisions. By colliding, the particles exchange their mechanical properties with the matrix or bath of the remaining particles representing the system, the local thermodynamic properties of which are defined by the external constraints. Permanent interaction of this matrix with the environment causes correlations between individual motions to disappear. The effect of collisions is to increase the resistance opposed by the system to flows.

The theory relies on the hard sphere mutual interaction model. This implies further the definition of an effective temperature dependent collision diameter for the different particles involved. The theory is clearly not suitable for predicting this quantity. It requires trajectory calculations based on the particular inter-particle interaction potentials. The question is well documented elsewhere [16]. In the treatment presented above, this problem has been bypassed by focussing on results obtained at constant temperature.

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FIG. 1. Predicted viscosity of a mixture of Xe in He, with $\epsilon = 0.98$ (smooth curve) and published experimental data (temperature: 291 K). The dotted curve is for $\epsilon = 1$.

FIG. 2. Predicted thermal conductivity of a mixture of Xe in He taking $c = 0.5$ (smooth curve) and published experimental data (temperature: 291 K). The dotted curves are for $c = 0$ and $c = 1$

TABLE I. List of the main constraints for Couette flow (distance between the walls: $2D$)

X_r	$\phi_r(\Gamma)$	ξ_r
Particles number	1	α
2nd moment of particle distribution	$[(z/D)^2 - 1]$	θ_2
Kinetic energy	$\sum(\frac{p^2}{2m})$	$-\beta$
2nd moment of energy distribution	$[(\frac{z}{D})^2 - 1] \sum(\frac{p^2}{2m})$	$-\gamma_2$
Gradient of shear momentum	$(z/D) p_y$	σ_y

TABLE II. List of the main constraints for thermal conductivity (distance between the walls: $2D$)

X_r	$\phi_r(\Gamma)$	ξ_r
Particles number	1	α
Gradient of particle distribution	(z/D)	θ_1
Kinetic energy	$\sum(\frac{p^2}{2m})$	$-\beta$
Gradient of energy distribution	$(z/D) \sum(\frac{p^2}{2m})$	$-\gamma_1$
Collective transverse momentum	p_z	σ_z

TABLE III. Correction ϵ to the heterogeneous collision diameter of pairs of gases, obtained by fitting the viscosity of the relevant mixtures to experimental data (temperature: 291 K)

	Ne	Ar	Kr	Xe
He	1.03	1.01	1.00	0.97
Ne		0.98	0.98	0.98
Ar			1.03	1.00
Kr				0.99

TABLE IV. Correction c to the partial pressure of the pairs of gases, caused by unrelaxed thermal diffusion, obtained by fitting the predicted thermal conductivity to experimental data (temperature: 291 K)

	Ne	Ar	Kr	Xe
He	0	0.7	0.55	0.5
Ne		0.5	1	1
Ar			1	1
Kr				1